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Wettability measurement of materials for ophthalmic applications

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Summary. — The wettability properties of materials for ophthalmic applications have been investigated through the contact angle technique. Measurements have been carried out on ophthalmic lenses with differing optical power but coated with the same multilayer or with differing multilayer treatments but equal optical power, under different cleaning conditions. Contact lenses of differing materials, both gas-permeable and soft, were also tested *in vitro*.

PACS `42.79.Bh` – Lenses, prisms and mirrors.
PACS `68.08.-p` – Liquid-solid interfaces.
PACS `82.70.Uv` – Surfactants, micellar solutions, vesicles, lamellae, amphiphilic systems, (hydrophilic and hydrophobic interactions).

1. – Introduction

The significant technological developments together with the increased market demand have made a wide set of ophthalmic materials available, differing by properties, quality and price [1, 2]. In particular, the wettability properties of contact lenses are altogether different from those of eyeglasses.

For contact lenses, wettability plays a large role in lens comfort, primarily due to its influence on tear film stability. Contact lens surface has to be hydrophilic, that is a *fluid-loving* surface where fluids spread over. The success of any contact lens implies the ability of the tear film to spread and maintain itself over its surface. General clinical consensus is that failure to meet this requirement is likely to result in a lens that is uncomfortable, has a reduced visual performance, and deposits rapidly [3].

On the contrary, surface of ophthalmic lenses has to be treated to become hydrophobic. Such a surface is *fluid fearing* and has the tendency to push the fluid away, minimizing the contact area. Nowadays, thermoplastic and thermosetting polymers are mainly used as the lens substrate. On the top of the substrate, a multipurpose multicoating is deposited. First, a hard coating is needed as anti-scratch since polymers are soft from the mechanical point of view. Then an antireflective (AR) multilayer can be useful to

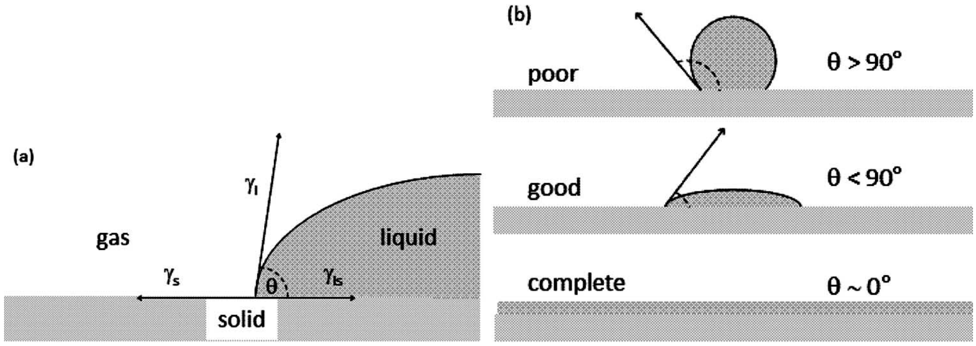

Fig. 1. – (a) Young's force diagram that introduces the notion of contact angle (θ) in macroscopic fluid mechanics. (b) Wetting degree of a surface from poor to complete related to contact angle values.

greatly reduce the light loss in multielement lenses by making use of phase changes and of the reflectivity dependence on index of refraction. Finally, a hydro/oleophobic thin film prevents liquids, smudges, finger prints and dust from adhering to the lens surface, eliminating potential visual distortion. The manufacturers' offer depends on the cost/quality ratio.

The wettability properties of materials for ophthalmic applications have been investigated making use of the contact angle technique.

2. – Wettability

Wettability of a solid substrate is influenced by three forces: the solid-air surface tension, the liquid-air surface tension, and the solid-liquid interfacial tension. When a drop is deposited on a solid surface, it will attempt to balance the system by minimizing the interfacial energy. Young already in 1805 proposed a description of this phenomenon [4] considering the forces along the three lines of contact (fig. 1(a)), according to

$$\gamma_l \cos\theta = \gamma_s - \gamma_{sl}, \tag{1}$$

where γ_l is the (liquid) surface tension, θ is the contact angle (CA), γ_s is the solid surface tension and γ_{sl} is the solid-liquid interfacial tension. The lower the contact angle is, the more the liquid is wetting the surface (fig. 1(b)).

It has to be pointed out that the terms wettability and contact angle are not synonyms, even though they are often used interchangeably [5]. Wettability cannot be related to a surface via the contact angle alone, as different liquids of differing surface tensions will give rise to different contact angles on a given solid surface. Indeed, wettability is a property of a liquid-solid combination rather than that of the solid surface alone.

3. – Experimental techniques

A sophisticated goniometer, Krüss DSA 100 [6], was used for contact angle measurements (fig. 2(a)). In principle, the instrument consists of four components:

– the sample table with three mobile axes;

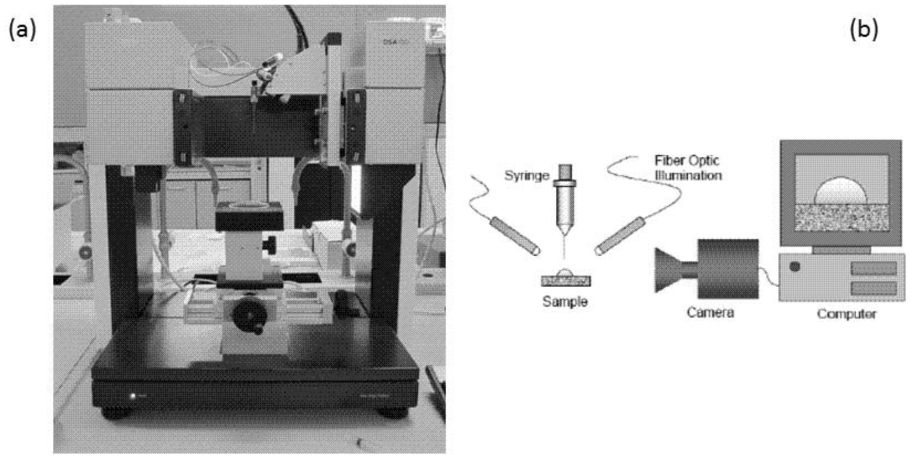

Fig. 2. – (a) The Krüss DSA100 goniometer; (b) sketch of the experimental setup.

– the video system with camera, optical system, prism, light source and aperture;

– a software-controlled dosing system;

– a software-controlled image analysis.

Its features are a 25 fps video camera, a 7× zoom/focus manual system, a contact angle range from 0° to 180° with an accuracy of 0.1°, and sample dimensions up to 300 × 150 mm^2. A sketch of the experimental setup is shown in fig. 2(b). Measurements have been carried out with two static methods (*sessile drop* and *captive bubble*). Static measurements are appropriate when inhomogeneities are to be determined. Mapping the sample—measuring the static contact angle at many sample positions—helps to provide a meaningful correlation between position and wettability.

3˙1. *Sessile drop*. – A liquid (deionized water) is deposited at room temperature on the lens to be tested in air. In fig. 3(a), a drop is shown before being deposited on the ophthalmic lens. The deposited drop can be photo-taken and/or video-recorded.

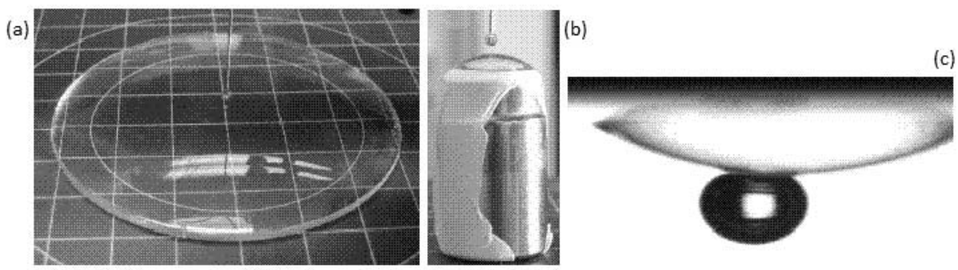

Fig. 3. – A *sessile drop* on an ophthalmic lens (a) and on a contact lens (b); (c) an air *captive bubble* deposited beneath a contact lens. Contact angle is the supplement of *bubble angle*.

The prism can vary the viewing angle of the drop without having to change the drop location and without any image distortion. The liquid volume is software-controlled by the operator. The drop volume is limited by the weight of the liquid itself, since this causes drop shape distortions. The surface tension γ_l of the liquid and the volume-dependent drop weight ρg determine the maximum drop radius which is represented by the capillary length κ^{-1} m

$$\kappa^{-1} = \sqrt{\frac{\gamma_l}{\rho g}}, \tag{2}$$

due to the equilibrium between the Laplace pressure and the hydrostatic pressure [7]. For water, this results in a maximum radius of 2.7 mm. Kranias [8] showed that between 1 μl and 10 μl no influence of drop weight could be demonstrated as a distortion factor.

In this study, drops were dosed to a maximum of 5 μl, so the effect of apparent increased wettability can be neglected (together with the uncertainty on the volume dose).

3·2. *Captive bubble*. – The lens to be tested is immersed in a liquid (deionized water). Instead of a drop, an air bubble is deposited beneath (fig. 3 (c)). The angle measured with respect to the bubble shape is said *bubble angle*. The contact angle is the supplement of the *bubble angle*.

3·3. *Software analysis*. – Drop images are analysed using the embedded Drop Shape Analysis (DSA) software.

Contact angles can be measured in real time or off-line on saved pictures. In the first step the drop image is subjected to a grey level analysis. The result is an optically determined contour around the phase boundary in the drop image. In the second step the drop contour is described mathematically. The contact angle is obtained from the angle between this drop contour function and the sample surface whose projection in the drop image is known as the *baseline*. The mathematical description of the *baseline* depends on its shape: a straight line equation for a flat surface, a circular function for rounded substrates. Several models are available for the analysis of the drop shape. In the *circle method*, a drop shape in the form of a circular arc is assumed. This requirement is fulfilled to a large extent by very small contact angles and drop volumes. The *Young-Laplace model* uses a sophisticated iterative method to take into account the drop deformation exerted by gravity. It is the most adopted, when the measuring range is above 30°. For *captive bubble* measurements, the drop shape is evaluated with the *tangent* method according to a generic conic section [9].

4. – Materials and methods

4·1. *Ophthalmic Lenses*. – All the measured ophthalmic lenses are made of CR-39, the plastic material that represents the largest category of lenses sold worldwide [10].

A first set of *sessile drop* measurements was carried out on three uncoated lenses (*blanks*) and on three lenses with the same super-hydrophobic treatment (SH), of differing dioptric power (+0.25, +1 and +3 D, respectively).

Wettability was mapped on each lens at five positions: center (C), top (U), bottom (D), right (R), and left (L), as shown in fig. 4. The mapped points are at a distance of 4 mm from the center. Each CA measurement is actually the mean of 20–30 CA values measured in 2-3 s. Mean values of CA in the center position are listed in table I.

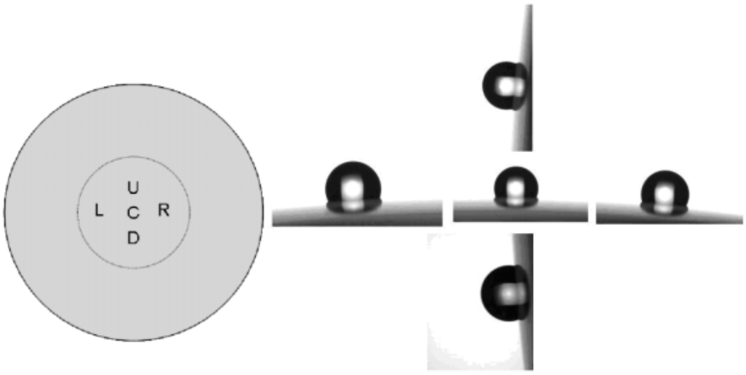

Fig. 4. – *Sessile drop* measurements are taken at center (C), top (U), bottom (D), left (L) and right (R) position on a 4 mm radius lens area. Drop pictures are shown for each position.

A second set was taken on five lenses with differing coatings of two different manufacturers. For convenience, the two manufacturers are listed by letters A and B. All A and B lenses have spherical geometry, a dioptric power of +2 D and refractive index of 1.5. A_1 is coated only by a hard coating, while A_2, B_1, B_2 and B_3 lenses are coated with an AR multilayer of increasing quality (and cost). Also for this set, wettability was mapped in five positions, in a 4 mm radius central area. Moreover, for each point, CA was measured every 60 s for 3 min to check the interaction with the surrounding environment. Three minutes is a time reasonably longer than that needed by the wearer to dry the lens in case, for example, of rain drops. CA was measured on unclean lenses and after cleaning with a commercial spray suitable for AR coatings. As an example, fig. 5 shows contact angle values as a function of position and time.

Mean values of CA in the center position (at 0 s) are listed in table I together with the quoted values in the marketing literature.

4·2. *Contact Lenses*. – Three Rigid Gas Permeable (RGP) and three soft contact lenses of differing materials were measured, making use of *sessile drop* and *captive bubble*

Table I. – *To the left, contact angles of three uncoated (blanks) and three super-hydrophobic (SH) CR-39 lenses with differing optical power* $(+0.25, +1, +3\,\mathrm{D})$. *To the right, contact angles of five CR-39 lenses with the same optical power* $(+2\,\mathrm{D})$ *but differing coatings, made by two manufacturers (M). Measurements were taken on unclean lenses and after cleaning with a commercial spray. Quoted values in the marketing literature are reported as available, without uncertainty and method declaration.*

	CA (°) *blank*	CA (°) SH	M	Coating	Price (euro)	CA (°) quoted	CA (°) unclean	CA (°) clean
+0.25	59.0 ± 0.1	107.8 ± 0.2	A_1	hard	30–40	–	84.9 ± 0.1	–
+1	68.7 ± 0.5	111.1 ± 0.1	A_2	AR	40–50	–	75.6 ± 0.3	–
+3	64.1 ± 0.1	107.2 ± 0.1	B_1	AR +	50–60	110	111.9 ± 0.2	109.6 ± 0.2
			B_2	AR ++	70–80	113	109.0 ± 0.3	112.8 ± 0.1
			B_3	AR +++	90–110	116	106.9 ± 0.2	110.5 ± 0.3

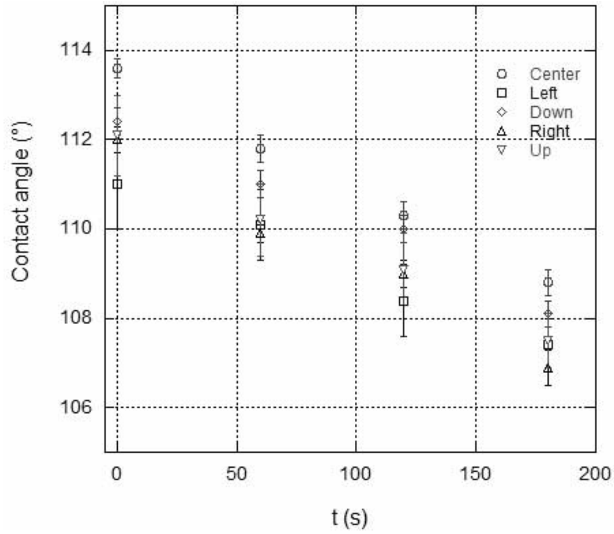

Fig. 5. – *Sessile drop* measurements taken at center (C), top (U), bottom (D), left (L) and right (R) position on a 4 mm radius lens area as a function of time. Data are for B_1 lens after cleaning.

techniques. The main properties are listed in table II. For the *sessile drop* method, the lenses were evaluated direct from their packaging solution (*i.e.*, surface active agents, if any, present). Each lens was removed with silicone-tipped tweezers (at the very edge of the lens only) from its blister, and repeatedly placed with the test (front) surface in contact with a microfibre cloth until any excess surface liquid had been removed. This typically required three separate placements and took about 10 s. The convex front surface of a custom-made lens holder was placed in direct contact with the upwards-facing back surface of the contact lens and lifted up such that the lens centered onto the holder without any lens handling. CA was measured only on the lens apex (fig. 3(b)).

For *captive bubble* measurements, lenses were placed onto a custom-made lens holder placed in a water-filled glass chamber that housed a curved needle from which an air bubble was dispensed (fig. 3(c)). The mean values of CA are listed in table II together with the quoted values in the marketing literature.

Table II. – *Contact angles of three RGP and three soft contact lenses. Quoted values in the marketing literature are reported as available, without uncertainty and method declaration.*

Contact lens	Material	Dk units	H_2O (%)	CA (°) quoted	CA (°) *sessile drop*	CA (°) *captive bubble*
RGP_1	enflufocon a	18	–	52	85.2 ± 0.1	44.9 ± 0.1
RGP_2	roflufocon b	26	–	12	83.1 ± 0.1	52.5 ± 0.6
RGP_3	hexafocon a	100	–	49	91.7 ± 0.1	69 ± 5
$SOFT_1$	enfilcon	100	46	37	38 ± 2	27 ± 5
$SOFT_2$	lotrafilcon b	110	33	37	13 ± 1	36 ± 1
$SOFT_3$	comfilcon a	128	48	30	23 ± 2	55 ± 1

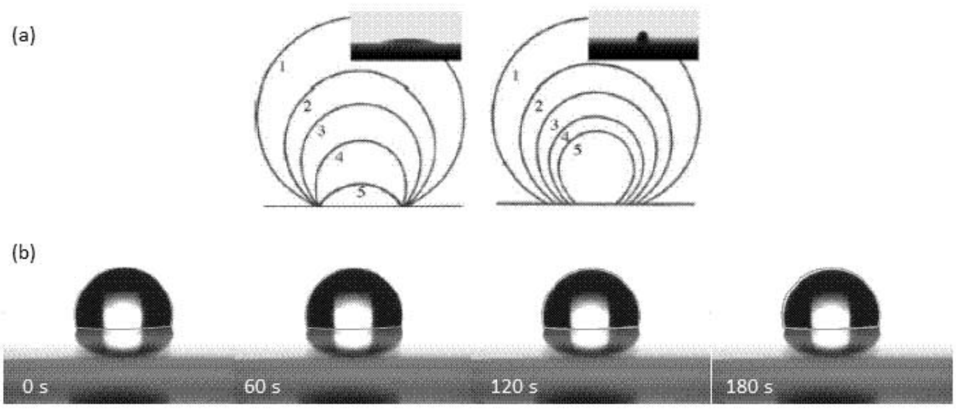

Fig. 6. – (a) Schematic shape evolution of water drop during evaporation: at constant contact radius (left) and at constant contact angle (right) [12]; (b) CA measurement on lens B_1 at time 0, 60, 120, 180 s. Diameter is constant while contact angle decreases linearly.

5. – Data analysis

5˙1. *Ophthalmic Lenses*. – On the first set of lenses, CA measures indicate that there is a clear difference between *blanks* and SH lenses, as desired. SH lenses show CA always greater than 107°, as expected, while CA for *blanks* are less than 69°. On the contrary, optical power does not seem to influence strongly wettability response.

As reported, static measurements are appropriate when inhomogeneities are to be determined. From this point of view, measuring CA at different positions means to investigate if the surface treatment on ophthalmic lenses is homogeneous. It is then necessary to statistically test if the CA mean values at top/bottom/right/left/center are equal. The analysis of variance (ANOVA) [11] showed that CA values are not equal nor for the *blanks* neither for the SH lenses (but for the +0.25 D lens). This means that the bulk polymer properties are locally dependent, as expected, and the super-hydrophobic treatment becomes less uniform and homogeneous increasing the optical power.

The same comparison was done for A and B lenses, before and after cleaning. In all cases, values were not found statistically equal: the coating (hard for A_1, AR for all the other lenses) is not homogeneous. The probability that mean values are comparable is $p < 0.0001$ for all tests. Moreover, for B lenses, the AR multilayer quality is not always worth the price. Lenses B_1 and B_2 are less wettable for unclean and cleaned lenses, respectively, even if cheaper than lens B_3. CA measured values are more comparable with quoted values for lenses B_1 and B_2.

On the second set of ophthalmic lenses, CA was studied also as a function of time to check interaction with the surrounding environment. Figure 5 shows that contact angle decreases linearly in each position due to evaporation. Literature reports that evaporation can be at constant contact angle or at constant contact radius [12] for initial values of contact angle greater or lower than 90°, respectively (fig. 6(a)). Evaporation is then expected to be at constant contact angle for lenses B, being the CA $> 90°$ at time 0 s. In particular, evaporation rate was analyzed for lens B_1, before and after cleaning. Pictures of the same size (640×480 pixels) were acquired at 0, 60, 120 and

180 s to check contact diameter. Contact diameter does not change while contact angle decreases during the three minutes measurement (fig. 6(b)). Data can only be considered as preliminary. Indeed, it was not possible to monitor temperature and humidity during the three-minutes-long measurement, so not all the variables could be under control. It has to be checked if the CA decrease is really significant on longer periods (2000–3000 s), as reported in the literature. From a practical point of view, it is however very probable that lens wearer dries eyeglasses within few minutes.

5·2. *Contact Lenses.* – There are inherent difficulties in obtaining static measurements on contact lenses. In the *sessile drop* case, during the measurement the material dries changing its properties. This is particularly dramatic for soft contact lenses. Moreover, surface active agents, if any, can interfere. Surface active agents are included in the blister solution to reduce the possibility of the lens sticking to the blister and additionally to enhance the initial on-eye wettability of the lenses. For the *sessile drop* technique, surface active agents change the water surface tension; for *captive bubble* case, the air bubble adhesion can be impeded.

As for RGP lenses, *sessile* CA values are always greater than *captive* ones. For soft lenses, the difference is lower. Agreement with quoted values (without uncertainty) is poor especially for *sessile drop* measurements.

The difference between *sessile drop* and *captive bubble* values is reported in the literature about silicone-hydrogel lenses, putting in evidence the dependence of measurement on methodology [3]. It can be explained by the rotational mobility of macromolecules at lens surface [13]. When the polymer segments of the hydrogel are subjected to an asymmetric molecular force field at the hydrogel-air interface, it is energetically more favorable to orientate the hydrophobic side groups towards the air and the hydrophilic sites within the hydrogel. On the contrary, when such a surface is immersed in water, that is a polar liquid, the polymer segments reorientate (with the hydrophobic side chains within the polymer) to achieve minimal interfacial tension. As a consequence, surface is more hydrophobic in case of *sessile* technique than in case of *captive* one.

6. – Conclusions

Using the sophisticated goniometer Krüss DSA 100 the wettability of lenses, of differing optical power with same surface treatment and of same optical power but differing surface treatment, was measured by the *sessile drop* technique. The static measurements are used to verify the uniformity of surface treatment, comparing the values of contact angles at various positions where measurements were taken. The average values in the five points are not compatible, as resulted by the ANOVA analysis, showing a non-uniform treatment in the central region of 4 mm radius. Only the lens with super-hydrophobic treatment and the lowest dioptric power (+0.25 D) passed the test.

The contact angle decreases linearly with time, as verified by the measurements on the second set of ophthalmic lenses. Evaporation occurs at variable contact angle and constant contact diameter, as it should instead be for initial CA values below 90°. The assessment can only be preliminary because the observation period of 180 s is less than 2000–3000 s, as normally reported in the literature.

For contact lenses, there is an inherent difficulty of evaluating the contact angle *in vitro*. In *sessile drop* mode, the materials tend to dry quickly, so it is difficult to determine if the measure is significant. Immersed in the solution, the presence of active surface agents can prevent the adhesion of the air bubble. The values of contact angle are dependent on the methodology and the comparison with the quoted values is limited by the fact that the manufacturers' contact angles are reported without uncertainty and indication of the measurement method. The difference between the *sessile drop* and *captive bubble* values can be justified considering the rotational kinetic energy of the macromolecules at the surface of the lenses.

For completeness, it is reported that the current legislation (UNI EN ISO 18369-3/4 2007) does not require the measurement of wettability to a standard accepted internationally, even though the usefulness of these measurements is recognized by the scientific community and widely advertised by the manufacturers.

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